

# (12) UK Patent Application (19) GB (11) 2 344 596 (13) A

(43) Date of A Publication 14.06.2000

(21) Application No 9827127.3

(22) Date of Filing 09.12.1998

(71) Applicant(s)  
E. I. Du Pont De Nemours and Company  
(Incorporated in USA - Delaware)  
1007 Market Street, Wilmington, Delaware,  
United States of America

(72) Inventor(s)  
William Alasdair Macdonald

(74) Agent and/or Address for Service  
Carpmaels & Ransford  
43 Bloomsbury Square, LONDON, WC1A 2RA,  
United Kingdom

(51) INT CL<sup>7</sup>  
C09K 21/12 , C08L 67/00

(52) UK CL (Edition R )  
C3V VDF VDM  
C3W W314  
U1S S1574

(56) Documents Cited  
US 4278591 A  
WPI Abstract Accession No. 1997-197345 [18] &  
JP 090053007 A WPI Abstract Accession No.  
1995-380229 [49] & JP 070258520 A WPI Abstract  
Accession No. 1981-08591D [06] & JP 550154161 A  
WPI Abstract Accession No. 1993-339845 [43] &  
JP 050247239 A

(58) Field of Search  
UK CL (Edition R ) C3V VDM  
INT CL<sup>7</sup> C08K 5/49 , C09K 21/00 21/12  
ONLINE: EPODOC, JAPIO, WPI.

(54) Abstract Title  
Flame retarded and UV light stabilised polyester film

(57) A polyester film, such as polyethylene terephthalate (PET) or polyethylene naphthalate (PEN), comprising at least one flame retardant and at least one UV light absorber. The flame retardant is an aromatic phosphorous containing compound. The UV light absorber is a triazine such as hydroxyphenyltriazine or metal oxide, such as titanium dioxide or zinc oxide. The polyester film may comprise a heat sealable layer. Further the polyester film may be co-extruded and stretched and is suitable for use as a protective layer on a metal sheet.

GB 2 344 596 A

Fig.1.

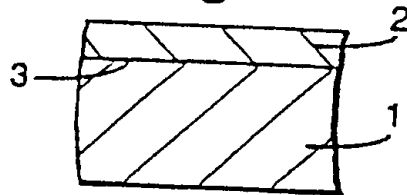


Fig.2.

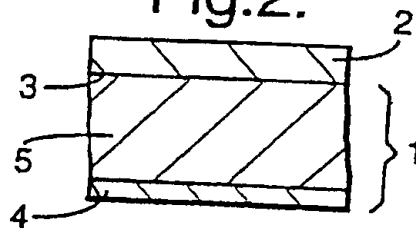
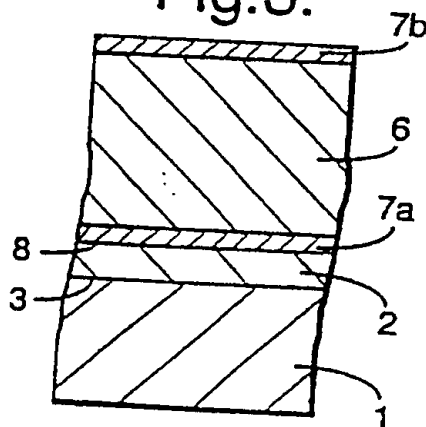


Fig.3.



POLYESTER FILM

This invention relates to a polymeric film which comprises a flame retardant additive and an ultra violet (UV) light absorber.

5

Most polymeric materials used in construction, textiles, furnishing and electrical applications are flammable and there is a strong desire to decrease the combustibility of materials and to render the materials safer in use. The most common approach is to add one or more flame retardant elements to the flammable polymer system but in turn these can cause other problems. Commonly these additives are based on antimony or bromine compounds, but there is an increasing environmental pressure to move away from flame retardant chemicals of this type. Halogen-containing flame retardants for example can release toxic fumes when exposed to high temperatures. Furthermore these chemicals often have to be added at loadings of 10-20%. The use of known flame retardants at such high levels can adversely affect subsequent processing and/or the physical properties of the compounded polymer composition.

Flame retardants which are non-halogenated and which are substantially antimony-free are known. Aromatic phosphate oligomers, such as resorcinol bisdiphenyl phosphate (RDP), have been used at various concentrations as flame retardants in polymer compositions, including poly(butylene terephthalate) (PBT), as described in European Patent Applications EP-A-0491986 and EP-A-0685518. Melamine pyrophosphate (MPP) is also known to be useful as a flame retardant in polyester compositions, as described in US-4278591, US-5618865 and US-5708065. The combination of MPP and a liquid aromatic phosphate oligomer such as RDP is disclosed in US-5814690 as improving the flame retardant properties of thermoplastic moulding compositions comprising PBT. JP-A-09/111100 discloses aromatic organophosphorus compounds of formula  $[(ArO)_2P(O)O]_2X$  (Ar = phenyl, optionally substituted; X = phenylene, naphthalene or biphenylene, optionally substituted) and their use in the preparation of polyester films.

Polyester films generally exhibit a lack of stability to UV radiation. This lack of stability manifests itself in a yellowing, hazing and cracking of the polyester on

exposure to sunlight, which has limited the potential use of the film in an outdoor environment.

It is known to increase the stability of polymers such as polyesters to UV light by the incorporation therein of a UV absorbing material. A UV absorber has an extinction coefficient much higher than that of the relevant polymer such that most of the incident UV light is absorbed by the UV absorber rather than by the polymer. The UV absorber generally dissipates the absorbed energy as heat, thereby avoiding degradation of the polymer chain. As a consequence, the stability of the polymer to UV light is increased.

For certain applications it is desirable to have films which exhibit both flame retardancy and UV stability, but at the same time retain the properties such as mechanical properties, strength and clarity that are associated with conventional films which do not contain flame retardants and UV stabilisers.

Accordingly, the present invention provides a polymeric film comprising a polyester film substrate comprising at least one UV absorber and at least one flame retardant compound.

The invention also provides a process for producing a polymeric film which comprises forming a substrate by extruding a layer of molten polyester comprising at least one UV absorber and at least one flame retardant compound, quenching the extrudate, optionally orienting the quenched extrudate in at least one direction and optionally forming a heat-sealable layer on a surface of the substrate.

The invention further provides a polymeric film comprising a polyester film substrate comprising at least one UV absorber and at least one flame retardant compound, and a heat-sealable layer on a surface of the substrate.

The polymeric films of the present invention which comprise a heat-sealable layer may be utilised in the coating of metal sheets. Metal sheet, in coil or plate form, needs to be coated with protective layers in order for it to possess adequate corrosion

resistance. Generally paint layers, or polymeric films such as polyvinyl chloride (PVC), or a combination of the two have been used to coat metal sheet. Polymeric films have certain advantages over paint layers, such as hardness, weatherability and aesthetic appearance. For certain applications of coated metal sheet, polymeric films may  
 5 possess insufficient weatherability, particularly when metal sheet is exposed to sunlight, for example when used as external cladding for buildings, and in other applications, may possess unacceptably high flammability.

The invention further provides use of a polymeric film comprising a polyester  
 10 film substrate, at least one UV absorber, at least one flame retardant compound and a heat-sealable layer on a surface of the substrate, as a protective coating layer on a metal sheet.

The invention still further provides a laminated metal sheet comprising (i) a  
 15 metal sheet, (ii) an optional primer layer, (iii) a paint layer, and (iv) a polymeric film comprising a polyester film substrate comprising at least one UV absorber, at least one flame retardant compound and a heat-sealable layer on a surface of the substrate, the heat-sealable layer being in contact with the paint layer.

20 The polyester film substrate is a self-supporting film by which is meant a self-supporting structure capable of independent existence in the absence of a supporting base. The thickness of the polyester substrate may vary over a wide range but preferably is within the range from 5 to 300  $\mu\text{m}$ , more preferably 10 to 100  $\mu\text{m}$ , particularly 12 to 50  $\mu\text{m}$ , and especially 12 to 30  $\mu\text{m}$ .

25

A polyester suitable for use in the formation of a substrate layer is preferably a synthetic linear polyester and may be obtained by condensing one or more dicarboxylic acids or their lower alkyl (up to 6 carbon atoms) diesters, e.g. terephthalic acid, isophthalic acid, phthalic acid, 2,5-, 2,6- or 2,7-naphthalenedicarboxylic acid, succinic  
 30 acid, sebacic acid, adipic acid, azelaic acid, 4,4'-diphenyldicarboxylic acid, hexahydro-terephthalic acid or 1,2-bis-p-carboxyphenoxyethane (optionally with a monocarboxylic acid, such as pivalic acid) with one or more glycols, particularly an aliphatic or cycloaliphatic glycol, e.g. ethylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl

glycol and 1,4-cyclohexanedimethanol. A polyethylene terephthalate (PET) or polyethylene naphthalate film is preferred. A polyethylene terephthalate film or a copolymer thereof is particularly preferred, especially such a film which has been biaxially oriented by sequential stretching in two mutually perpendicular directions, typically at a temperature in the range from 70 to 125°C, and preferably heat set, typically at a temperature in the range from 150 to 250°C, for example as described in GB-A-838708.

The polyester substrate may be unoriented, or preferably oriented, for example uniaxially oriented, or more preferably biaxially oriented by drawing in two mutually perpendicular directions in the plane of the film to achieve a satisfactory combination of mechanical and physical properties. Simultaneous biaxial orientation may be effected by extruding a thermoplastics polymeric tube which is subsequently quenched, reheated and then expanded by internal gas pressure to induce transverse orientation, and withdrawn at a rate which will induce longitudinal orientation. Sequential stretching may be effected in a stenter process by extruding the thermoplastics material as a flat extrudate which is subsequently stretched first in one direction and then in the other mutually perpendicular direction. Generally, it is preferred to stretch firstly in the longitudinal direction, i.e. the forward direction through the film stretching machine, and then in the transverse direction. A stretched substrate film may be, and preferably is, dimensionally stabilised by heat-setting under dimensional restraint at a temperature above the glass transition temperature thereof.

In principle, any flame retardant suitable for use with polyester-containing compositions may be employed in the present invention. It is preferred that non-halogenated and substantially antimony-free flame retardants are used, preferably a phosphorus-based flame retardant, and more preferably an aromatic organophosphorus compound.

Suitable examples of flame retardants for use in the present invention include those disclosed in US-4278591, US-5618865, US-5708065, EP-A-0491986, EP-A-0685518 and JP-A-09/111100. The teaching of the aforementioned patent specifications is incorporated herein by reference. Examples of commercially-available

flame retardants which are suitable for use in the present invention are Fyrolflex™ RDP and Antiblase™ 1045.

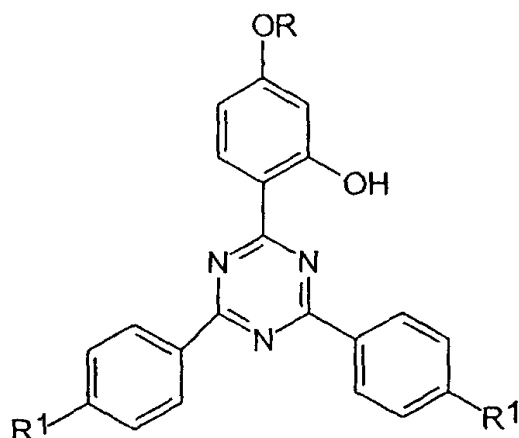
The amount of flame retardant present in the polyester substrate is preferably in  
5 the range from 0.1% to 45%, more preferably from 0.1% to 30% and more preferably from 5% to 15% by weight relative to the weight of the polyester.

Where the flame retardant is a phosphorus-containing flame retardant, the  
amount of flame retardant present in the polyester substrate, by weight of phosphorus  
10 relative to the weight of the polyester, is preferably in the range from 0.05% to 10%, more preferably 0.05% to 5%, more preferably 0.1% to 4% and particularly 0.4 to 2%.

In principle, any organic or inorganic UV absorber suitable for use with  
polyester may be employed in the present invention. Suitable examples include the  
15 organic UV absorbers disclosed in Encyclopaedia of Chemical Technology, Kirk-Othmer, Third Edition, John Wiley & Sons, Volume 23, Pages 615 to 627. Particular examples of UV absorbers include benzophenones, benzotriazoles (US-4684679, US-4812498 and US-4681905), benzoxazinones (US-4446262, US-5251064 and US-5264539) and triazines (US-3244708, US-3843371, US-4619956, US-5288778 and WO  
20 94/05645). The teaching of the aforementioned documents is incorporated herein by reference.

In one embodiment of the invention, the UV absorber may be chemically  
incorporated in the polyester chain. Preferred UV-stable polyesters are produced by  
25 incorporating benzophenones into the polyester, for example as described in EP-A-0006686, EP-A-0031202, EP-A-0031203 and EP-A-0076582, the teaching of which is incorporated herein by reference.

Triazines are preferred UV absorbers, more preferably hydroxyphenyltriazines,  
30 and particularly hydroxyphenyltriazine compounds of Formula 1:



(1)

wherein R is hydrogen, C<sub>1</sub>-C<sub>18</sub> alkyl, C<sub>2</sub>-C<sub>6</sub> alkyl substituted by halogen or by C<sub>1</sub>-C<sub>12</sub> alkoxy, or is benzyl and R<sup>1</sup> is hydrogen or methyl. R is preferably C<sub>1</sub>-C<sub>12</sub> alkyl or benzyl, more preferably C<sub>3</sub>-C<sub>6</sub> alkyl, and particularly hexyl. R<sup>1</sup> is preferably hydrogen. An especially preferred UV absorber is 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyl)oxy-phenol, which is commercially available as Tinuvin<sup>TM</sup> 1577 FF from Ciba-Additives.

10

Suitable inorganic UV absorbers include metal oxide particles, such as zinc oxide or titanium dioxide, having a mean crystal size, as determined by electron microscopy, of less than 200 nm, more preferably in the range from 5 to 150 nm, particularly 10 to 100 nm, and especially 15 to 40 nm. Titanium dioxide particles are particularly preferred.

15

The titanium dioxide particles may be of anatase or rutile crystal form. The titanium dioxide particles preferably comprise a major portion of rutile, more preferably at least 60% by weight, particularly at least 80%, and especially approximately 100% by weight of rutile. The particles can be prepared by standard procedures, such as using the chloride process or preferably by the sulphate process.

20

In one embodiment of the invention the titanium dioxide particles are coated, preferably with inorganic oxides such as aluminium, silicon, zinc, magnesium or



mixtures thereof. Preferably the coating additionally comprises organic compound(s), such as fatty acids and preferably alkanols, suitably having from 8 to 30, preferably from 12 to 24 carbon atoms. Polydiorganosiloxanes or polyorganohydrogensiloxanes, such as polydimethylsiloxane or polymethylhydrogensiloxane are suitable organic  
5 compounds.

The coating is suitably applied to the titanium dioxide particles in aqueous suspension. The inorganic oxides are precipitated in aqueous suspension from water-soluble compounds such as sodium aluminate, aluminium sulphate, aluminium  
10 hydroxide, aluminium nitrate, silicic acid or sodium silicate.

Suitable titanium dioxide particles are commercially available, for example Tiosorb<sup>TM</sup> ultra-fine titanium dioxide particles from Tioxide, UK.

15 The amount of UV absorber present in the polyester substrate is preferably in the range from 0.1% to 10%, more preferably 0.2% to 7%, more preferably 0.6% to 4%, particularly 0.8% to 2%, and especially 0.9% to 1.2% by weight, relative to the weight of the polyester.

20 In one embodiment of the invention, both an organic UV absorber, preferably a triazine, and an inorganic UV absorber, preferably titanium dioxide, are present in the polyester substrate. The ratio, by weight of inorganic to organic UV absorber is preferably in the range from 0.5 to 10:1, more preferably 1 to 5:1, and particularly 1.5 to 2.5:1.

25 Particularly improved aesthetic appearance occurs when the external surface of the polyester substrate is matt, preferably exhibiting a 60° gloss value, measured as herein described, of less than 60%, more preferably in the range from 5% to 55%, particularly 20% to 50%, and especially 35% to 45%.

30 The external surface of the polyester substrate suitably exhibits a root mean square surface roughness (Rq), measured as herein described, of greater than 50,

preferably in the range from 200 to 1500 nm, more preferably 400 to 1200 nm, and particularly 500 to 1000 nm.

5 In order to obtain the preferred properties of the polyester film substrate surface it may be necessary to incorporate relatively small quantities of filler material therein. Suitable fillers include inorganic materials such as silica, china clay, glass, mica, calcium carbonate, and organic materials such as silicone resin particles. Spherical monodisperse fillers may be employed. Silica is a particularly preferred filler.

10 The concentration of filler particles present in the substrate is preferably in the range from 0.001% to 5%, more preferably 0.05% to 3%, particularly 0.5% to 2%, and especially 0.8% to 1.2% by weight, relative to the weight of the polyester.

15 The filler particles preferably have a volume distributed median particle diameter (equivalent spherical diameter corresponding to 50% of the volume of all the particles, read on the cumulative distribution curve relating volume % to the diameter of the particles – often referred to as the “D(v,0.5)” value), as determined by laser diffraction, in the range from 0.3 to 20  $\mu\text{m}$ , more preferably 1 to 10  $\mu\text{m}$ , particularly 3 to 8  $\mu\text{m}$ , and especially 5 to 7  $\mu\text{m}$ .

20 Particle size of the filler particles described herein may be measured by electron microscope, coulter counter, sedimentation analysis and static or dynamic light scattering. Techniques based on laser light diffraction are preferred. The median particle size may be determined by plotting a cumulative distribution curve representing the percentage of particle volume below chosen particle sizes and measuring the 50th percentile. The volume distributed median particle diameter of the filler particles is suitably measured using a Malvern Instruments Mastersizer MS 15 Particle Sizer after dispersing the filler in ethylene glycol in a high shear (e.g. Chemcoll) mixer.

30 The components of the polymer film substrate composition may be mixed together in a conventional manner. For example, by mixing with the monomeric reactants from which the polyester is derived, or the components may be mixed with the polyester by tumble or dry blending or by compounding in an extruder, followed by

cooling and, usually, comminution into granules or chips. The UV absorber and/or the flame retardant may be fed separately to the extruder from which the polyester is extruded to form the substrate layer. Alternatively masterbatch technology, i.e. the addition of an additive in concentrate form in an appropriate polymer, may be employed.

The haze (% of scattered transmitted visible light) of the polymeric film is measured according to the standard ASTM D 1003-61. An unfilled film according to the present invention desirably has a haze of <6%, more preferably <3.5% and particularly <1.5%. A typical unfilled film according to the present invention having a film thickness of 20 $\mu$ m has a haze of 0.1 to 1.5%. A typical unfilled film according to the present invention having a film thickness of 75 $\mu$ m has a haze of 1.5 to 4%. A typical filled film according to the present invention having a film thickness of 20 $\mu$ m has a haze of 2.5 to 5% (for example, using a filler of china clay at approximately 0.155% w/w). A typical filled film according to the present invention having a film thickness of 75 $\mu$ m has a haze of 12 to 20% (for example, using a filler of china clay at approximately 0.155% w/w).

The polymeric films of the present invention may optionally comprise a heat-sealable layer on a surface of the substrate, as mentioned above.

The heat-sealable layer is preferably a polymeric coating layer which is capable of forming a heat-seal bond to itself and/or to the polyester substrate and/or to the metal sheet as described herein, by heating to soften the polymeric material of the heat-sealable layer and applying pressure without softening or melting the polyester material of the substrate layer. The heat-sealable layer preferably exhibits a heat-seal strength, measured by sealing the layer to itself, in the range from 200 to 3000, more preferably 300 to 1500, and particularly 350 to 500 Nm<sup>-1</sup>.

In a preferred embodiment of the invention the heat-sealable layer suitably comprises a polyester resin, particularly a copolyester resin derived from one or more dibasic aromatic carboxylic acids, such as terephthalic acid, isophthalic acid and hexahydroterephthalic acid, and one or more glycols, such as ethylene glycol,

diethylene glycol, triethylene glycol and neopentyl glycol. Typical copolyesters which provide satisfactory properties are those of ethylene terephthalate and ethylene isophthalate, especially in the molar ratios of from 50 to 90 mole % ethylene terephthalate and correspondingly from 50 to 10 mole % ethylene isophthalate.

5 Preferred copolyesters comprise from 65 to 85 mole % ethylene terephthalate and from 35 to 15 mole % ethylene isophthalate, and especially a copolyester of about 82 mole % ethylene terephthalate and about 18 mole % ethylene isophthalate.

The heat-sealable layer may be applied from an organic or aqueous solvent to an

10 already oriented polyester substrate or, more preferably, before or during the stretching operation. Alternatively, the heat-sealable layer may be formed by casting the heat-sealable polymer onto a preformed substrate layer. Conveniently, however, formation of a composite sheet (substrate and heat-sealable layer) is effected by coextrusion, either by simultaneous coextrusion of the respective film-forming layers through independent

15 orifices of a multi-orifice die, and thereafter uniting the still molten layers, or, preferably, by single-channel coextrusion in which molten streams of the respective polymers are first united within a channel leading to a die manifold, and thereafter extruded together from the die orifice under conditions of streamline flow without intermixing thereby to produce a composite sheet.

20

A coextruded sheet is stretched to effect molecular orientation of the substrate, and preferably heat-set. Generally, the conditions applied for stretching the substrate layer will induce partial crystallisation of the heat-sealable polymer and it is therefore preferred to heat set under dimensional restraint at a temperature selected to develop the

25 desired morphology of the heat-sealable layer. Thus, by effecting heat-setting at a temperature below the crystalline melting temperature of the heat-sealable polymer and permitting or causing the composite to cool, the heat-sealable polymer will remain essentially crystalline. However, by heat-setting at a temperature greater than the crystalline melting temperature of the heat-sealable polymer, the latter will be rendered

30 essentially amorphous. Heat-setting of a composite sheet comprising a polyester substrate and a copolyester heat-sealable is conveniently effected at a temperature within a range of from 175 to 200°C to yield a substantially crystalline heat-sealable

layer, or from 200 to 250°C to yield an essentially amorphous heat-sealable layer. An essentially amorphous heat-sealable layer is preferred.

5 The thickness of the heat-sealable layer may vary over a wide range but generally will not exceed 50  $\mu\text{m}$ , and is preferably in the range from 0.5 to 30  $\mu\text{m}$ , more preferably 2 to 15  $\mu\text{m}$ , and particularly 3 to 10  $\mu\text{m}$ .

10 In one embodiment of the present invention, the polyester film substrate is a multilayer film, preferably having two layers, a first outer layer, and a second inner layer. Where a heat-sealable layer is present, it is the second, inner layer which is in contact with the heat-sealable layer. The chemical composition of the outer and inner substrate layers is preferably the same, more preferably of polyethylene terephthalate or a copolymer thereof. The ratio of the thickness of the outer layer to the thickness of the inner layer is preferably in the range from 0.02:1 to 1:1, more preferably 0.05:1 to 0.5:1, 15 particularly 0.1:1 to 0.3:1, and especially 0.15:1 to 0.25:1.

A least one, and preferably each, layer of a multilayer film comprises a flame retardant compound.

20 The concentration of UV absorber present in the outer substrate layer is preferably in the range from 0.5% to 10%, more preferably 1% to 8%, particularly 3% to 7%, and especially 4% to 6% by weight, relative to the weight of the polyester. The inner substrate layer preferably comprises substantially no UV absorber or significantly smaller amounts of UV absorber than are present in the outer substrate layer. In a 25 particular preferred embodiment of the present invention, the inner substrate layer comprises in the range from 1% to 40%, more preferably 3% to 25%, particularly 5% to 20%, and especially 10% to 15% by weight of UV absorber, relative to the amount of UV absorber present in the outer substrate layer. It is preferred that the same UV absorber(s) is/are present in both the outer and inner substrate layers.

30

The concentration of filler particles present in the outer substrate layer is preferably in the range from 0.001% to 5%, more preferably 0.05% to 3%, particularly 0.5% to 2%, and especially 0.8% to 1.2% by weight, relative to the weight of the

polyester. The inner substrate layer preferably comprises substantially no filler particles or significantly smaller concentrations of filler than are present in the outer substrate layer.

- 5           A polymeric film comprising an outer polyester substrate layer, an inner polyester substrate layer and optionally a heat-sealable layer is preferably formed by coextrusion as described herein.

10           The layers of the polymeric film according to the present invention may, if desired, contain any of the additives conventionally employed in the manufacture of polymeric films. Thus, agents such as dyes, pigments, voiding agents, lubricants, anti-oxidants, anti-blocking agents, surface active agents, slip aids, gloss-improvers, prodegradants, viscosity modifiers and dispersion stabilisers may be incorporated as appropriate.

15           The polymeric film according to the present invention is particularly suitable for use as a protective coating on a metal sheet, particularly when applied to the metal sheet on a coil coating line, for example as described in EP-A-0686501, the teaching of which is incorporated herein by reference. Suitable metal sheets include cold rolled steel, 20   metallised steel, stainless steel, galvanised steel, and aluminium etc.

          The metal sheet may be chemically pretreated, e.g. by the known methods of chromating, pickling and phosphatising, prior to the optional application of a standard primer coat. The thickness of the dried primer coat is preferably in the range from 2 to 25   30  $\mu\text{m}$ , more preferably 5 to 20  $\mu\text{m}$ .

          A pigmented or non-pigmented paint layer can be applied either directly, or by means of the primer layer, to the metal sheet. Conventional paints may be used, such as acrylic, polyester, fluorocarbon dispersions, PVC-plastisols, vinyl or latex paints. The 30   thickness of the dried paint layer is preferably in the range from 5 to 120  $\mu\text{m}$ , more preferably 15 to 80  $\mu\text{m}$ , particularly 25 to 60  $\mu\text{m}$ , and especially 30 to 50  $\mu\text{m}$ .

The primer or paint layer may be applied by conventional techniques such as doctor blade coating, roller coating, spray coating or curtain coating.

5 The polymeric film according to the present invention may be adhered, by means of the heat-sealable layer, to the painted metal sheet by conventional laminating techniques, such as by using a pressure roller or calendering. The polymeric film is preferably applied to a hot paint surface, e.g. whereby the painted metal sheet has been heated in an oven at a temperature in the range from 200 to 230°C.

10 The invention is illustrated by reference to the following drawings in which:

Figure 1 is a schematic sectional elevation, not to scale, of a polymeric film having a polyester film substrate and a heat-sealable layer.

15 Figure 2 is a similar schematic elevation of a film shown in Figure 1, wherein the polyester film substrate is a two layer film having an outer layer and an inner layer .

Figure 3 is a similar schematic elevation of a film shown in Figure 1, bonded to a painted metal sheet.

20

Referring to Figure 1 of the drawings, the polymeric film comprises a polyester film substrate (1) having a heat-sealable layer (2) bonded to a surface (3) of the substrate.

25 The film of Figure 2 has a polyester film substrate (1) having two layers, an outer layer (4) and an inner layer (5) bonded to the heat-sealable layer (2).

The film of Figure 3 additionally comprises a metal sheet (6) having painted outer layers (7a and 7b) bonded to the surface (8) of the heat-sealable layer (2).

30

The following test methods are used to determine certain properties of the polymeric film:

- (i) Haze is measured using a Hazegard System XL-211, according to ASTM D 1003-61.
- (ii) 60° gloss value of the film surface is measured using a Dr Lange Reflectometer REFO 3 (obtained from Dr Bruno Lange, GmbH, Dusseldorf, Germany) according to  
5 DIN 67530.
- (iii) The root mean square roughness (Rq) of the external surface of the polyester film substrate is measured using a Wyko Optical Profiler over a field of view of 0.9 x 1.2 mm.
- (iv) Heat-seal strength of the heat-sealable layer is measured by positioning together  
10 and heating two heat-sealable layers present on polyester film substrate layers at 140°C for one second under a pressure of 275 kPa (40 psi). The sealed film is cooled to room temperature, and the heat-seal strength determined by measuring the force required under linear tension per unit width of seal to peel the layers of the film apart at a constant speed of 4.23 mm/second.
- (v) The polyester film is tested in an Atlas C165 Weather-ometer under the  
15 following conditions: automatic irradiance of 0.35 Wm<sup>2</sup> at 340 nm, black panel temperature = 63°C (theoretical maximum temperature), wet bulb depression = 10°C, conditioning water = 30°C, weathering cycle = 102 minutes light/18 minutes water, time of test = 1000 hours. The ultimate tensile strength (UTS) of the film is measured  
20 (kgmm<sup>2</sup>) after testing and expressed as a percentage of the original value.

The invention is further illustrated by means of the following Examples.

## 25 Examples

In all of the examples, a phosphorus content of 0.8% w/w (by weight relative to the weight of the polyester) was obtained by blending a Crystar<sup>TM</sup> 3998 flame resist PET resin containing 10% flame retardant (RDP) concentrate with PET containing  
30 0.15% slip additive. Tinuvin<sup>TM</sup> 1577F at 1% level was obtained by further blending a 10% masterbatch with the above two polymer compositions.

The polymer composition was dried in air for 6 hours at 150°C before being extruded through a twin screw extruder on a pilot plant scale film line.



Temperatures along the barrel were set at 275°C. The screw speed was determined by a gear pump suction/delivery control loop so as to provide a constant flow of melt through the die. The pump speed was fixed at 28rpm. Melt temperatures exiting the die were between 285 and 290°C depending on output, i.e. film thickness.

Three film thicknesses were made by altering casting drum speed, slow and fast roll speed in the forward draw (machine direction) with stenter speed being determined by fast roll speed. The films were 20, 36 and 75 micron thick and had a forward draw ratio of 3.2 and a sideways draw ratio of 3.3. These samples are labelled 1, 2 and 3. Samples 4 and 5 are control films and contain no flame retardant or UV stabiliser.

Test samples, 200 mm x 50 mm, were cut from each film sample and formed into tubes 200 mm long by 13 mm diameter. Two test samples from each film sample were used in the testing. There was no conditioning of the samples. A line was drawn 75 mm from the top of the tubes. Before flame application the top of each tube was held shut by a spring clamp which, with a stand, held the test sample vertical. Closing one end of the tube prevented chimney effects during flame application. A burner flame was adjusted to produce a blue flame  $20 \pm 1$  mm. Continuous adjustment of the propane supply and the air port was necessary to achieve the correct height.

The film tube was held vertically and the flame applied to the bottom of the tube 10 mm below the film. Flame application was for 3 seconds, maintaining the 10mm distance by moving the burner upwards as the film shrank away from it. After 3 seconds the flame was moved away from the sample and the duration (in seconds) of flaming after the first flame application noted (A). A repeat 3 second application was completed and the duration (in seconds) of flaming after the second flame application (B) and the duration (in seconds) of flaming plus glowing after the second flame application (C) noted. If a specimen burned to the 75 mm mark, observation D was yes. During the flame application if any drips of molten polymer fell from the sample, observation E was yes. Results are shown in Table 1.

**Table 1**

<b>Sample</b>	<b>Thickness</b>	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>	<b>E</b>
<b>1</b>	20 $\mu\text{m}$	0	1	1	no	yes
		0	0	0	no	no
<b>2</b>	36 $\mu\text{m}$	0	1	1	no	yes
		0	1	1	no	yes
<b>3</b>	75 $\mu\text{m}$	0	0	0	no	no
		0	0	0	no	no
<b>4</b>	19 $\mu\text{m}$	4	1	0	no	yes
		13	1	0	no	yes
<b>5</b>	75 $\mu\text{m}$	3	2	1	no	yes
		15	3	0	no	yes

- 5 The results indicate that the polymer films of the present invention self-extinguish after primary ignition.

CLAIMS

1. A polymeric film which comprises a polyester film substrate comprising at least one flame retardant compound and at least one UV absorber.  
5
2. A film according to claim 1 wherein the flame retardant compound is non-halogenated and substantially antimony-free.
3. A film according to claim 2 in which the flame retardant compound comprises phosphorus.  
10
4. A film according to claim 3 in which the flame retardant compound comprises an aromatic phosphorus-containing compound.
- 15 5. A film according to any of the preceding claims wherein the polyester substrate comprises from 0.1% to 45% by weight, relative to the weight of the polyester, of the flame retardant compound.
6. A film according to claim 3 or 4 wherein the polyester substrate comprises from 0.05% to 10% by weight of phosphorus relative to the weight of the polyester, of the phosphorus-containing flame retardant compound.  
20
7. A film according to any of the preceding claims which self-extinguishes after ignition.  
25
8. A film according to any of the preceding claims wherein the polyester substrate comprises at least two coextruded layers.
9. A film according to any of the preceding claims wherein the polyester substrate comprises 0.1-10% by weight, relative to the weight of the polyester, of the UV absorber.  
30

10. A film according to any of the preceding claims wherein the UV absorber compound comprises a triazine.
11. A film according to any of claims 1-10 wherein the UV absorber comprises a metal oxide.
12. A film according to any of the preceding claims wherein the polyester substrate comprises polyethylene terephthalate (PET) or a copolymer thereof.
13. A film according to any preceding claim further comprising a heat-sealable layer on a surface of the substrate.
14. A process for producing a polymeric film which comprises forming a substrate by extruding a layer of molten polyester comprising at least one UV absorber and at least one flame retardant compound, quenching the extrudate, optionally orienting the quenched extrudate in at least one direction and optionally forming a heat-sealable layer on a surface of the substrate.
15. A process according to claim 14 further comprising the step of mixing a polyester polymer with a masterbatch comprising a polyester polymer and at least one flame retardant compound prior to extrusion.
16. A process according to claim 14 further comprising the step of adding at least one flame retardant compound to a polymer condensate prior to extrusion.
17. Use of the film according to claim 13 as a protective coating layer on a metal sheet.
18. A laminated metal sheet comprising (i) a metal sheet, (ii) an optional primer layer, (iii), a paint layer, and (iv) a polymeric film comprising a polyester film substrate comprising at least one UV absorber, at least one flame retardant compound and a heat-resealable layer on a surface of the substrate, the heat-sealable layer being in contact with the paint layer.



INVESTOR IN PEOPLE

Application No: GB 9827127.3  
Claims searched: 1-18

Examiner: Dr Albert Mthupha  
Date of search: 30 March 2000

## Patents Act 1977 Search Report under Section 17

### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.R): C3V (VDF, VDM)

Int CI (Ed.7): C08K (5/3492, 5/49); C09K (21/00, 21/12)

Other: ONLINE: EPODOC, JAPIO, WPI.

### Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	US 4278591 A AMERICAN CYANAMID, see column 1 lines 5-8, line 20-column 2 line 17, lines 36-44 & Claims 1, 4.	1-7, 9, 11 at least.
X	WPI Abstract Accession No. 1997-197345 [18] & JP 9053007 A (TEIJIN), see Abstract.	1-3, 7, 10 at least.
X	WPI Abstract Accession No. 1995-380229 [49] & JP 7258520 A (NIPPON), see Abstract.	1-4, 7, 11 at least
X	WPI Abstract Accession No. 1981-08591D [06] & JP 55154161 A (TOYOBO), see Abstract.	1, 7, 12 at least.
X	WPI Abstract Accession No. 1993-339845 [43] & JP 5247239 A (TEIJIN), see Abstract.	1 at least.

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

2000

1000

1000

1000

1000

1000

1000

1000

1000

